The New Superconductors

Frank J. Owens

Army Armament Research Engineering and Development Center
Picatinny, New Jersey
and Hunter College of the City University of New York
New York, New York

and

Charles P. Poole, Jr.

Institute of Superconductivity
University of South Carolina
Columbia, South Carolina

Plenum Press • New York and London

Library of Congress Cataloging-in-Publication Data

On file

ISBN 0-306-45453-X

A Division of Plenum Publishing Corporation
233 Spring Street, New York, N. Y. 10013

10 9 8 7 6 5 4 3 2 1

Printed in the United States of America

Table 8.1. Progress in Raising the Superconducting Transition Temperature T_c Since the Discovery of Cuprates in 1986

Material	T_c (K)	Year
$Ba_xLa_{5-x}Cu_5O_9$	30–35	1986
$(La_{0.9}Ba_{0.1})_2Cu_4O_{4-x}$ (at 1-GPa pressure)[a]	52	1986
$YBa_2Cu_3O_{7-x}$	95	1987
$Bi_2Sr_2Ca_2Cu_3O_{10}$	110	1988
$Tl_2Ba_2Ca_2Cu_3O_{10}$	125	1988
$Tl_2Ba_2Ca_2Cu_3O_{10}$ (at 7-GPa pressure)	131	1993
$HgBa_2Ca_2Cu_3O_{8+x}$	133	1993
$HgBa_2Ca_2Cu_3O_{10}$ (at 30-GPa pressure)	147	1994

[a]A pressure of 1 GPa is about 10,000 atm.

While this increase in T_c itself is an amazing result, a high-transition temperature is not the only property required to make new compounds useful for applications. For example if materials are to be used as wires in magnets, they must be malleable and ductile rather than brittle; in addition they must have high critical currents in large magnetic fields. Critical currents as high as those in niobium-tin have not yet been achieved in forms of the new materials that can easily be made into wires, although there are reports of comparable values in thin films on various substrates.

The Holy Grail that is being sought is a transition temperature much above room temperature. We say much above because devices must operate significantly below the transition T_c so that the critical current J_c and critical magnetic field B_c are sufficiently high. Very close to the transition temperature, the critical magnetic field is usually quite small, but we see from Figs. 3.4 and 3.5 that B_c and J_c continuously increase as the temperature is lowered below T_c. We need an operating temperature far below the critical surface in Fig. 3.15 so that both B_c and J_c are sufficiently large for the desired application.

8.3. LAYERED STRUCTURE OF THE CUPRATES

All cuprate superconductors have the layered structure shown in Fig. 8.1: The flow of supercurrent takes place in conduction layers, and binding layers support and hold together the conduction layers. Conduction layers contain copper-oxide (CuO_2) planes of the type shown in Fig. 8.2; each copper ion (Cu^{2+}) is surrounded by four oxygen ions (O^{2-}). These planes are held together in the structure by calcium (Ca^{2+}) ions located between them, as indicated in Fig. 8.3. An exception to this is the yttrium compound in which the intervening ions are the element yttrium (Y^{3+}) instead of calcium. These CuO_2 planes are very close to being flat. In the normal state above T_c, conduction electrons released by copper atoms move about on these

Transition Temperature T_c
n 1986

Year
1986
1986
1987
1988
1988
1993
1993
1994

t, a high-transition tempera-
npounds useful for applica-
s in magnets, they must be
ıey must have high critical
igh as those in niobium-tin
als that can easily be made
ues in thin films on various

n temperature much above
; must operate significantly
d critical magnetic field B_c
ature, the critical magnetic
.4 and 3.5 that B_c and J_c
w T_c. We need an operating
so that both B_c and J_c are

ES

ure shown in Fig. 8.1: The
ınd binding layers support
yers contain copper-oxide
r ion (Cu^{2+}) is surrounded
in the structure by calcium
.3. An exception to this is
the element yttrium (Y^{3+})
being flat. In the normal
toms move about on these

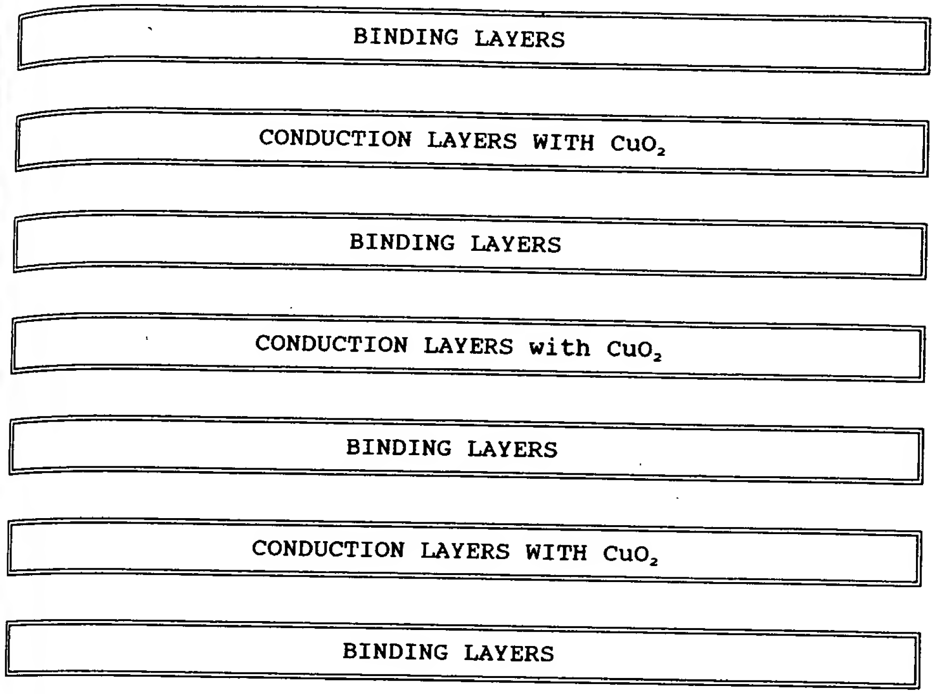


Figure 8.1. Layering scheme of the cuprate superconductors. Figure 8.3 shows details of the conduction layers for different sequences of copper oxide planes, and Fig. 8.4 presents details of the binding layers for several cuprates.

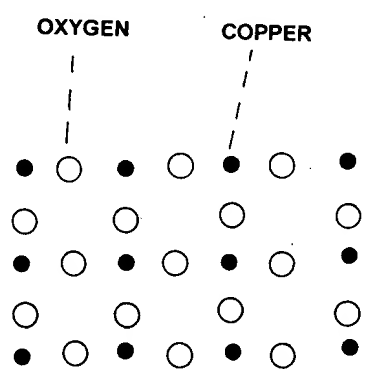


Figure 8.2. Arrangement of copper and oxygen atoms in a CuO_2 plane of the conduction layer.

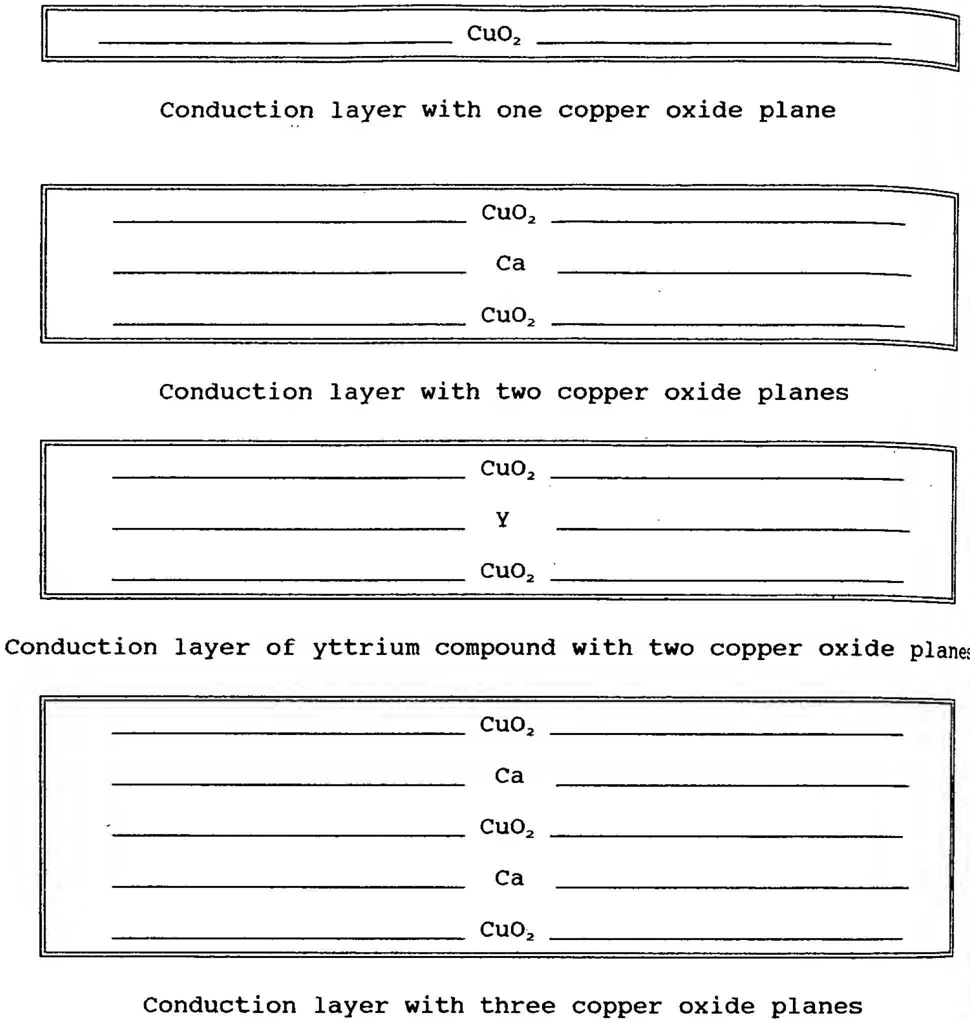
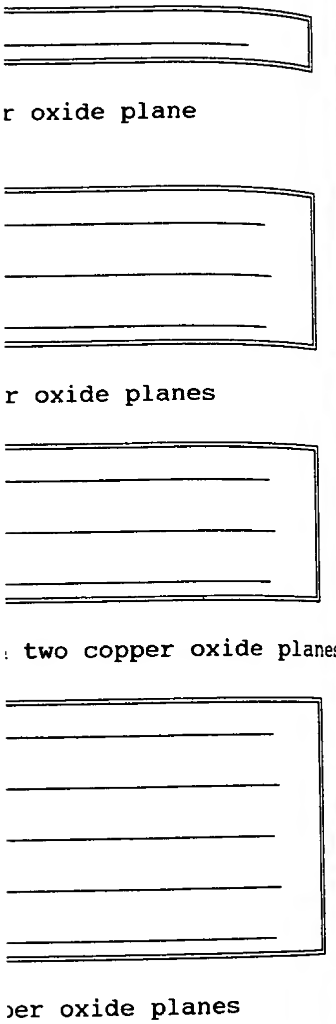


Figure 8.3. Conduction layers of the various cuprate superconductors showing sequences of CuO_2 and Ca (or Y) planes in the conduction layers of Fig. 8.1.

CuO_2 planes carrying electric current. In the superconducting state below T_c, these same electrons form the Cooper pairs that carry the supercurrent in the planes.

Each particular cuprate compound has its own specific binding layer consisting mainly of sublayers of metal oxides MO, where M is a metal atom; Fig. 8.4 gives the sequences of these sublayers for the principal cuprate compounds. These binding layers are sometimes called *charge reservoir layers* because they contain



ctors showing sequences of CuO_2 and

nducting state below T_c, these supercurrent in the planes. ecific binding layer consisting is a metal atom; Fig. 8.4 gives l cuprate compounds. These *ir layers* because they contain

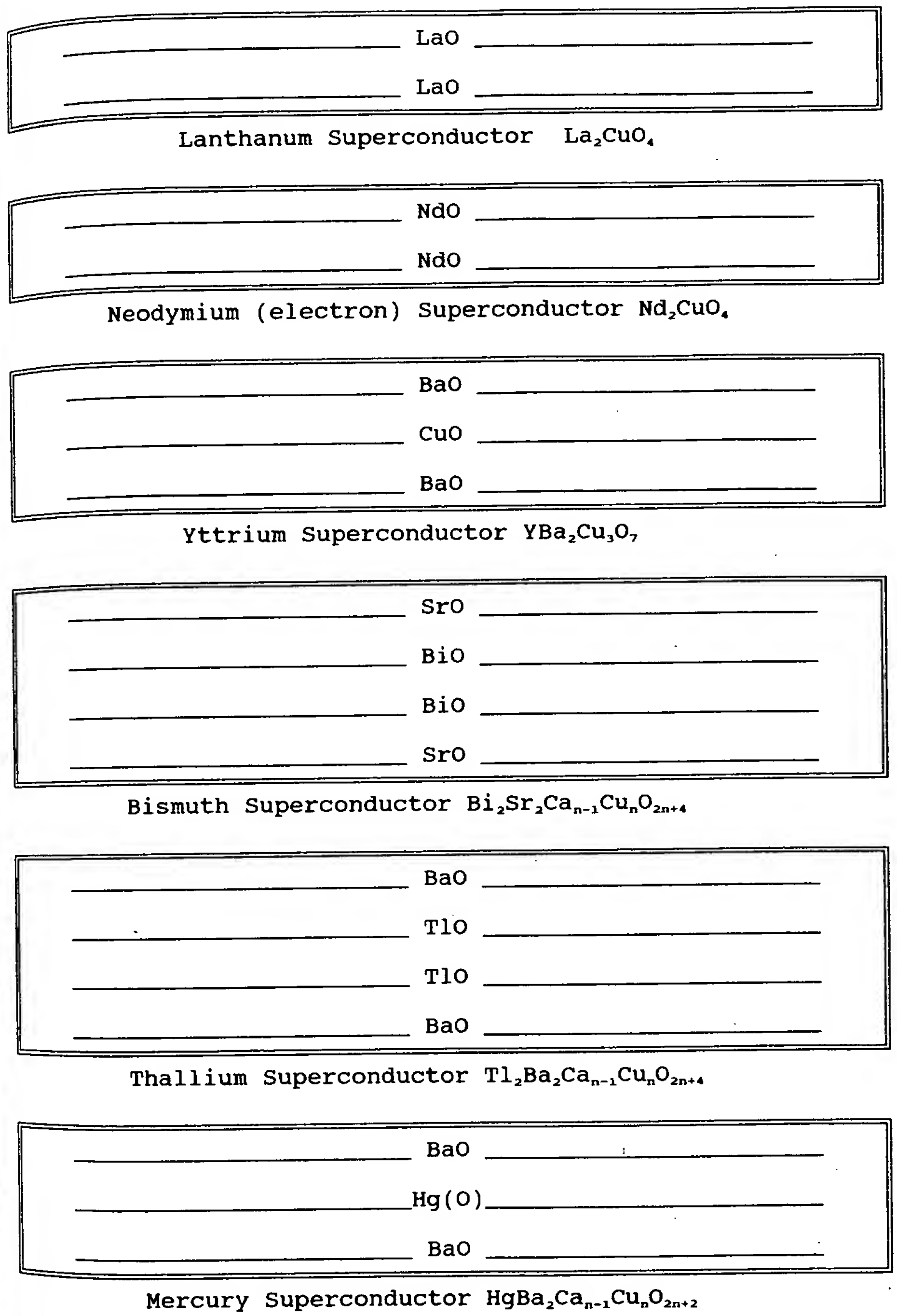


Figure 8.4. Sequences of MO sublayers in the binding layers of Fig. 8.1, where M stands for various metal ions. The parentheses around the oxygen atom O in the lowest panel indicates partial occupancy.

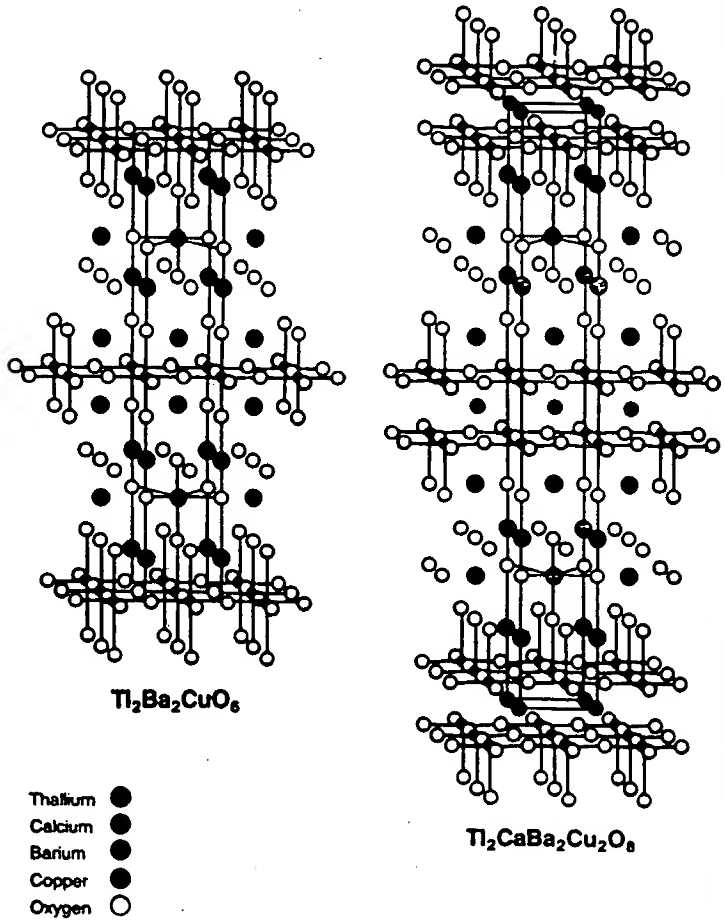


Figure 8.5. Layering schemes of three thallium compound superconductors $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+6}$, where there are n = 1, 2, 3 CuO_2 planes in the conduction layers, from left to right. [Adapted from Torardi et al., *Science* **240**, 631 (1988).]

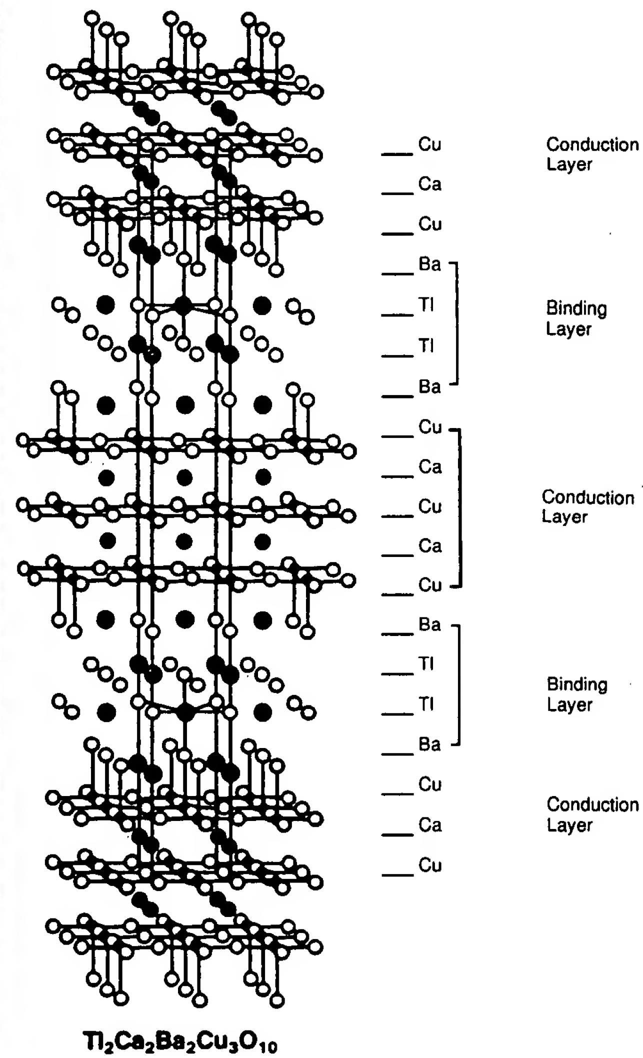


Figure 8.5. (Continued)

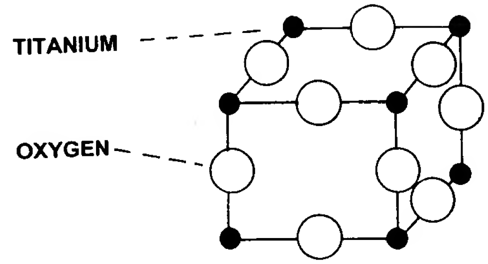


Figure 8.9. Sketch of the cubic unit cell of the mineral Perovskite, $CaTiO_3$, showing titanium at the vertices and oxygen in the middle of the edges. Calcium, not shown, is in the center of the cube.

In contrast the ceramic designation is not based on structural grounds but on the similarity of the cuprate-superconducting compound and ceramic manufacturing process. For example La-Sr-Cu-O is made by heating mixtures of lanthanum oxide, strontium carbonate, and copper oxide in air at 900–1000 °C for 20 hours. Proportions of atoms in the initial mixture should be the same as in the end product, and for the compound $(La_{0.9}Sr_{0.1})_2CuO_4$ the ratio La:Sr:Cu is 1.8:0.2:1. Materials are usually ground to a fine mixture before heating; after heating in air, they are cooled, pressed into pellets, and reheated from 900–1000 °C for several more hours.

We see in Fig. 8.10 that the superconductor $(La_{1-x}Sr_x)_2CuO_4$ has only one copper oxide plane in its conduction layer and each copper ion is surrounded by

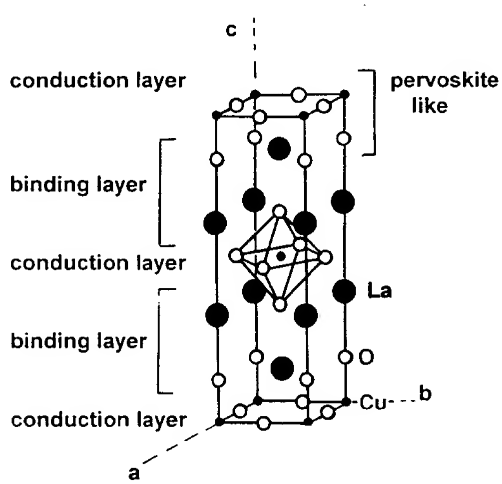


Figure 8.10. Atom positions in the tetragonal unit cell of the La_2CuO_4 compound. When strontium is substituted for lanthanum in the superconducting compound $(La_{1-x}Sr_x)_2CuO_4$ it replaces lanthanum in some of the La sites.

six neighboring oxygen ions; these form an 8-sided figure called an octahedron, as shown. The CuO_6 complex of one copper and six oxygens is present in all cuprate superconductors that have a single CuO_2 plane in their conduction layer. Figure 8.11 shows atom arrangements in the mercury compound $HgBa_2Ca_2Cu_3O_{10}$, which has three such planes in its conduction layer. In the upper and lower planes, copper ions have five neighboring oxygens forming a CuO_5 group with the shape of a pyramid, as shown. The middle copper ions have only four nearby oxygens, forming what is called a *square planar group* CuO_4. If we consider removing the central copper oxide plane and one calcium layer from Fig. 8.11, we generate the two-plane structure in which all copper ions form CuO_5 pyramids. These structural details may somehow constitute important factors in determining why cuprates are such good superconductors.

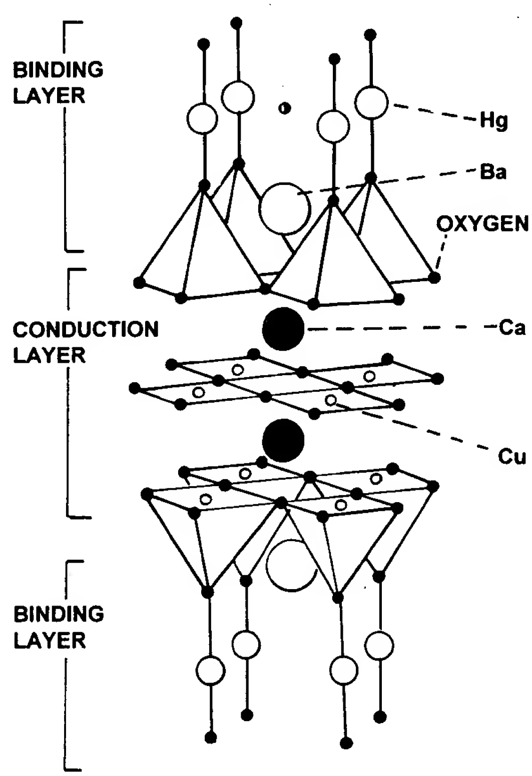


Figure 8.11. Atom positions in four unit cells of the superconducting compound $HgBa_2Ca_2Cu_3O_{8+x}$ which has $T_c = 133$ K. The copper ions of the upper CuO_2 plane are hidden by the pyramids, and some partially occupied oxygen sites in the mercury Hg plane are not shown.